

Proceedings of the American Academy of Arts and Sciences.

VOL. XXXVI. No. 5. — JULY, 1900.

---

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY  
OF HARVARD COLLEGE.

*CERTAIN*  
*DERIVATIVES OF METADIBROMDINITROBENZOL.*

BY C. LORING JACKSON AND W. P. COHOB.



CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.

CERTAIN DERIVATIVES OF METADIBROMDINITRO-  
BENZOL.

BY C. LORING JACKSON AND W. P. COHOE.

Presented December 13, 1899. Received June 4, 1900.

THE dibromdinitrobenzol melting at  $117^{\circ}.4$  was made by Körner in his classical research on Isomerism of the Aromatic Compounds with Six Atoms of Carbon,\* but its constitution has not been determined with certainty. Nietzki and Schedler † in a recent paper have proved that the dichlordinitrobenzol melting at  $103^{\circ}$  has the structure  $\text{Cl}_2.1.3.(\text{NO}_2)_2.4.6$ , and as this substance is made from the action of fuming nitric acid on metadichlorbenzol, just as the dibrom compound is made from metadibrombenzol, there is good reason to believe that they have the same constitution; but we thought it necessary to prove that this was the case before we studied this dibromdinitrobenzol further. For this purpose we heated the substance with aniline, and obtained the dianilidodinitrobenzol melting at  $186^{\circ}$ , which Nietzki and Schedler had obtained from their dichlordinitrobenzol; the dibrom substance therefore has the structure  $\text{Br}_2.1.3.(\text{NO}_2)_2.4.6$ . If aniline acted on the dibromdinitrobenzol in the cold, a bromanilidodinitrobenzol,  $\text{C}_6\text{H}_2\text{BrC}_6\text{H}_5\text{NH}(\text{NO}_2)_2$ , melting at  $157^{\circ}$  was obtained, and this occurs in a yellow and in a red modification which seem to differ in crystalline form as well as in color. This seems to be a case of dimorphism, as the two forms pass into each other with great ease. The yellow form is converted into the red by crystallization from benzol, the red into the yellow by heating to  $135^{\circ}$ . Similar phenomena have been observed in the cases of anilidotrinitrophenyltartronic ester ‡ and trianilidodinitrobenzol. §

---

\* Gazz. Chim. 1874, 305.

† Ber. d. chem. Ges., XXX. 1666 (1897).

‡ Jackson and Bentley, These Proceedings, XXVI. 83.

§ Jackson and Herman, Ibid. XXVII. 253.

After the constitution of the 1. 3. 4. 6 dibromdinitrobenzol had been determined, we studied the action of sodic ethylate upon it, in the hope of encountering the replacement of bromine by hydrogen under the action of this reagent, which has been studied for some years in this Laboratory. But no such behavior was observed; the action ran in the normal way, resulting in the formation of the dinitroresorcine diethylether melting at  $133^{\circ}$ , discovered by Warren and one of us,\* and proved to have the symmetrical structure by Koch and one of us †; so that this observation confirms the determination of the constitution of this body by the action with aniline.

Sodic phenylate converted the dibromdinitrobenzol into diphenoxydinitrobenzol, which melts at  $129^{\circ}$ . The action of sodic malonic ester was tried on this compound to determine whether the phenoxy groups could be replaced by the malonic ester radical  $\text{CH}(\text{COOC}_2\text{H}_5)_2$ ; as it has been found ‡ that the best way to make dichlordimalonicesterquinone  $\text{C}_6\text{Cl}_2[\text{CH}(\text{COOC}_2\text{H}_5)_2]_2\text{O}_2$  is by treating dichlordiphenoxyquinone with sodic malonic ester, and we wished to see whether the nitro groups would produce the same effect as the oxygen atoms of the quinone in promoting the replacement of the phenoxy groups by malonic ester radicals. We found that phenol was eliminated when the diphenoxydinitrobenzol was treated with sodic malonic ester, and from the very unmanageable product a sodium salt was obtained which contained an amount of sodium corresponding to  $\text{C}_6\text{H}_2\text{OC}_6\text{H}_5\text{CNa}(\text{COOC}_2\text{H}_5)_2(\text{NO}_2)_2$ ; so that we feel justified in assuming that the reaction has consisted in the replacement of the phenoxy by the malonic ester group.

The dibromdinitrobenzol, when reduced with zinc dust and acetic acid, gave a dibrommetaphenylene diamine, which was identical with that melting at  $135^{\circ}$  obtained by the action of bromine on metaphenylene diacetamid. § It follows from our preparation of this base that it has the constitution  $\text{Br}_2$  1. 3.  $(\text{NH}_2)_2$  4. 6.

In all this work we have been careful not to approach too near to the field reserved by Nietzki and Schedler in their paper on dichlordinitrobenzol.

---

\* These Proceedings, XXV. 170.

† Ibid. XXXIV. 134.

‡ Jackson and Grindley, Ibid. XXX. 425.

§ Jackson and Calvert, Ibid. XXXI. 150.

## PREPARATION OF METADIBROMDINITROBENZOL.

Monobromacetanilid was first made by passing a stream of air laden with the vapor of bromine through five litres of water in which fifty grams of acetanilid were suspended. The end of the reaction was determined by the appearance of a lasting yellow color in the liquid and a distinct change in the appearance of the solid. In all our attempts to convert this product into the dibromacetanilid by the action of liquid bromine on it when suspended in water, we observed the formation of a considerable amount of symmetrical tribromaniline ( $\text{NH}_2$  1. Br<sub>3</sub> 2. 4. 6.), produced undoubtedly by the action of bromine on the free base proceeding from the saponification of some of the bromacetanilid by the hydrobromic acid formed in the reaction. The monobromacetanilid was accordingly filtered out, and after being dried, suspended in glacial acetic acid or chloroform, to which a little more than the calculated amount of bromine was then added drop by drop. This method gave an excellent yield of the dibromacetanilid with little trouble.

The dibromacetanilid was saponified by boiling it with sulphuric acid of specific gravity 1.44 in a flask with a return condenser, until the solution of the solid, which was usually accompanied by a darkening in color, showed that the reaction was complete. The liquid was then allowed to cool, when most of the dibromaniline crystallized out, and what remained in solution was precipitated by the addition of a large quantity of water.

To remove the amido group, 100 grams of the dibromaniline were dissolved in a mixture of 300 c.c. of alcohol and 120 c.c. of benzol, to which 20 c.c. of sulphuric acid had been added; the mixture was heated in a flask on the steam bath, and 60 grams (a large excess) of solid sodic nitrite added as fast as the reaction would permit. The contents of the flask, which had taken on a reddish color, were boiled for an hour, and then allowed to stand over night, after which a large quantity of water was added, and the precipitated oily liquid distilled over with steam. A small amount of tribrombenzol is usually present, which appears as a solid in the condenser toward the end of the distillation with steam; it is well to stop the distillation as soon as this solid appears. The distillate with steam was dried with calcic chloride and distilled, collecting for use the fraction boiling from  $210^\circ$  to  $225^\circ$ . A small additional amount of dibrombenzol was obtained by extracting with ether the aqueous portion of the steam distillate, but the increase of the yield in this way was so small that this extraction was hardly worth while.

The dibrombenzol was converted into dinitrodibrombenzol by boiling

it with fuming nitric acid of specific gravity 1.52, or better a mixture of this acid and sulphuric acid. As soon as the oil had dissolved in the acid, the reaction was complete; the boiling was stopped, and the product precipitated by pouring the acid liquid into a large quantity of cold water. The yellow crystals thus obtained were purified by crystallization from alcohol, until they showed the constant melting point  $117^{\circ}$ .

DETERMINATION OF THE CONSTITUTION OF METADIBROMDINITRO-BENZOL BY THE ACTION OF ANILINE.

Two grams of the dibromdinitrobenzol melting at  $117^{\circ}$  were heated with an excess of aniline on the steam bath for half an hour. At the end of this time the excess of aniline was removed by treatment with dilute hydrochloric acid, and the yellow residue, after being washed thoroughly with water, was recrystallized from a mixture of alcohol and benzol until it showed the constant melting point  $185^{\circ}$ , which is essentially identical with  $186^{\circ}$ , that of the dianilidodinitrobenzol prepared from dichlorodinitrobenzol by Nietzki and Schedler.\* As they established the constitution  $(\text{NHC}_6\text{H}_5)_2$  1. 3.  $(\text{NO}_2)_2$  4. 6 for this body, the dibromdinitrobenzol melting at  $117^{\circ}$  must have the corresponding structure  $\text{Br}_2$  1. 3.  $(\text{NO}_2)_2$  4. 6.

ACTION OF ANILINE ON SYMMETRICAL DIBROMDINITROBENZOL IN THE COLD: BROMANILIDODINITROBENZOL.

Two grams of the dibromdinitrobenzol cooled by a freezing mixture were moistened with aniline, and the mixture was allowed to stand packed in ice for twelve to eighteen hours. The excess of aniline was then removed by dilute hydrochloric acid, and the dense yellow residue, after thorough washing with water, was purified by crystallization from alcohol and benzol until it showed the constant melting point of  $157^{\circ}$ , when it was dried at  $100^{\circ}$ , and analyzed, with the following result:—

- I. 0.0994 gram of the substance gave by the method of Carius 0.0558 gram of argentic bromide.
- II. 0.2138 gram of the substance gave 0.1229 gram of argentic bromide.

	Calculated for $\text{C}_6\text{H}_2\text{Br}_2\text{C}_6\text{H}_5\text{NH}(\text{NO}_2)_2$	I.	Found.	II.
Bromine	23.67	23.89		24.46

\* Ber. d. chem. Ges., XXX. 1668 (1897).

PROPERTIES OF BROMANILIDODINITROBENZOL,  
 $C_6H_2BrC_6H_4NH(NO_2)_2$  (Br 1.  $C_6H_4NH$  3.  $(NO_2)_2$  4. 6.).

This substance crystallizes from a mixture of benzol and alcohol, sometimes in much modified short and thick flat prisms apparently of the monoclinic system, resembling certain crystals of felspar; at other times in rhombic plates occasionally with some of the angles slightly bevelled, which pass into forms like rhombohedra; all of these crystals have a full golden yellow color. Other crystals were distinguished from these by their brilliant red color and by appearing in square prisms modified on one of their angles or on two opposite angles. From these two colors, red and yellow, and the difference at least in crystalline habit, if not really in crystalline form, we infer that the substance appears in two closely related modifications. The yellow form, in which the substance is obtained from its preparation, becomes gradually converted into the red by crystallization from a mixture of alcohol and benzol, but several crystallizations are necessary to make this conversion complete. If, however, the yellow form is dissolved in benzol alone, the solution deposits, as it evaporates, a red oil, which on stirring solidifies to the red crystals. All the other common organic solvents except the alcohols also convert the yellow into the red form by a single crystallization. On the other hand, if the red crystals are heated in an air bath, they begin to assume a yellow color at  $110^\circ$ , and are completely converted into the yellow form at  $135^\circ$ ; this conversion is attended with no change in weight. The substance melts at  $157^\circ$ , forming a red liquid, which, when cooled and stirred, solidifies to the yellow modification. It is obvious that the melting point given above is that of the yellow form, since the red is converted into the yellow at  $135^\circ$ . The bromanilidodinitrobenzol is freely soluble in benzol; soluble in toluol or chloroform; slightly soluble in ether, acetone, amyl alcohol, or hot ethyl alcohol. The best solvent for it is a mixture of benzol and alcohol.

DETERMINATION OF THE CONSTITUTION OF METADIBROMDINITROBENZOL BY TREATMENT WITH SODIC ETHYLATE.

One gram of the dibromdinitrobenzol melting at  $117^\circ$  was mixed with an excess of sodic ethylate prepared by the action of sodium on a considerable excess of absolute alcohol, and after the mixture had stood for some time at ordinary temperatures, the excess of alcohol was allowed to evaporate spontaneously. The residue, after repeated washings with

hot water, was purified by crystallization from a mixture of ligroin and benzol, when it was found to melt at  $133^{\circ}$ , the melting point of the dinitroresorcine diethylether discovered by Warren and one of us,\* which it also resembled in crystalline form. As Koch and one of us† have proved that this dinitroresorcine diethylether has the constitution  $(\text{OCH}_3)_2$  1. 3.  $(\text{NO}_2)_2$  4. 6, it follows that the dibromdinitrobenzol melting at  $117^{\circ}$  has the constitution  $\text{Br}_2$  1. 3.  $(\text{NO}_2)_2$  4. 6, — a result which confirms that already obtained from the action of aniline.

#### ACTION OF SODIC PHENYLATE WITH SYMMETRICAL DIBROMDINITRO-BENZOL.

The sodic phenylate for this experiment was prepared by adding five grams of powdered sodic hydrate to enough melted phenol to make a pasty mass. While this was still in the viscous state, five grams of the dibromdinitrobenzol were added little by little with constant stirring, the beaker containing the mixture being kept cool with ice water. The product, a dark brown solid mass, was treated with water, filtered, and the insoluble portion recrystallized either from slightly dilute alcohol, or from a mixture of benzol with a large excess of ligroin, until it showed the constant melting point  $129^{\circ}$ , when it was dried *in vacuo*, and analyzed, with the following results:—

- I. 0.2494 gram of the substance gave on combustion 0.5563 gram of carbonic dioxide and 0.0903 gram of water.
  - II. 0.3746 gram gave on combustion 0.8457 gram of carbonic dioxide.
- The water was unfortunately lost.

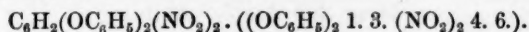
	Calculated for $\text{C}_6\text{H}_2(\text{OC}_6\text{H}_5)_2(\text{NO}_2)_2$ .	Found.	
		I.	II.
Carbon	61.38	60.82	61.59
Hydrogen	3.41	4.02	

The method of making sodic phenylate given above was adopted because in alcoholic solution the sodic phenylate gave principally the dinitroresorcine diethylether, and in aqueous solution there was no action until high temperatures were reached, and then the yield was unsatisfactory.

\* These Proceedings, XXV. 170.

† Ibid., XXXIV. 134.

## PROPERTIES OF THE DINITRORESORCINE DIPHENYLETHER,



This substance, when crystallized from a mixture of benzol and alcohol, forms slender white prisms terminated by one slanting plane, or, when better developed, by two planes meeting at a very obtuse angle and modified by several smaller ones, so that a blunt end is formed. It melts at  $129^\circ$ . It is freely soluble in benzol; soluble in cold toluol or chloroform, or in alcohol, ligroin, or acetone when these solvents are hot; slightly soluble in ether or amyl alcohol. The best solvent for it was either dilute alcohol, or ligroin containing a little benzol.

Some experiments were tried to determine whether the phenoxy groups in the diphenoxydinitrobenzol could be replaced by malonic ester radicals  $(\text{CH}(\text{COOC}_2\text{H}_5)_2)$ , as a replacement of this sort had been observed in the case of dichlordiphenoxyquinone.\* The solid diphenoxydinitrobenzol was dissolved in an alcoholic solution of sodic malonic ester, and the mixture allowed to stand at ordinary temperatures over night; afterward it was treated with dilute sulphuric acid, which precipitated an oil, and showed that phenol had been set free by the strong smell of this substance. The oily precipitate, after washing with water, was extracted with ether, which removed from it a pale yellow oily substance; but as this did not solidify even after standing for several months, we tried to determine its nature by the analysis of a salt. A specimen of the oil was dissolved in alcohol and treated with an aqueous solution of sodic hydrate, which threw down a bright red precipitate; this was washed with benzol, dried *in vacuo*, and analyzed, with the following results:—

- I. 0.1383 gram of the substance gave 0.0191 gram of sodic sulphate.  
 II. 0.1476 gram of the substance gave 0.0228 gram of sodic sulphate.

	Calculated for $\text{C}_6\text{H}_2(\text{NO}_2)_2\text{OC}_6\text{H}_5\text{CNa}(\text{COOC}_2\text{H}_5)_2$ .	I.	Found.	II.
Sodium	5.23	4.47		5.01

The results of these analyses, in connection with the elimination of phenol, prove that the reaction has run as was expected. The phenoxydinitrophenylmalonic ester separated from the salt as an oil, and therefore we did not think it worth while to attempt a more careful study of it.

\* Jackson and Grindley, These Proceedings, XXX. 425.

REDUCTION OF SYMMETRICAL DIBROMDINITROBENZOL WITH ZINC  
DUST AND ACETIC ACID.

Twenty grams of zinc dust were placed in a flask fitted with a Bunsen valve and connected with a carbonic dioxide generator, acetic acid of eighty-five per cent was added, and then five grams of the dibromdinitrobenzol in small portions at a time, as under these conditions the reaction ran quietly and smoothly, although accompanied by blackening in every case. The reduction was carried on at first in the cold, but toward the end of the operation the mixture was heated gently on the steam bath. After two hours the reaction was complete, when the insoluble portion was filtered out, and extracted with dilute alcohol, which upon cooling deposited crystals melting even in the crude state at  $131^{\circ}$ . The filtrate from the insoluble reduction products was treated with an excess of sodic hydrate sufficient to dissolve the zinc salts, the precipitate formed in this way filtered out, and extracted with hot dilute alcohol, which gave another portion of the crude product melting at  $131^{\circ}$ . After purification by crystallization from alcohol the melting point became constant at  $134^{\circ}$ ; it was dried *in vacuo*, and analyzed with the following result:—

0.1407 gram of the substance gave by the method of Carius 0.1976 gram of argentic bromide.

	Calculated for $C_6H_2Br_2(NH_2)_2$ .	Found.
Bromine	60.15	59.78

This dibromophenylene diamine melts essentially at the same point ( $135^{\circ}$ ) as that prepared by S. Calvert and one of us\* from metaphenylene diacetamide and bromine. It also crystallizes like this in white needles, which turn brown on exposure to the air. As the constitution of our dibrombinitrobenzol is  $Br_2$  1. 3.  $(NO_2)_2$  4. 6, it follows that this dibrommetaphenylene diamine must have the corresponding constitution  $Br_2$  1. 3.  $(NH_2)_2$  4. 6.

---

\* These Proceedings, XXXI. 150.

